ION-EXCHANGE STUDIES FOR USE IN ANALYSIS OF SOME DITHIOCARBAMATE FUNGICIDES

DISSERTATION

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By

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Dedicated

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Certificate

This is to certify that the dissertation entitled "Ion – Exchange Properties of Dithiocarbamate Fungicides" submitted for the degree of Master of Philosophy in Applied Chemistry, is a faithful record of the bonafide research work carried out at the Department of Applied Chemistry, Zakir Hussain College of Engineering and Technology, Aligarh Muslim University, Aligarh by Mrs. Charu Varshney under my guidance and supervision.

HSRathore

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Charu Varshney

Mrs. CHARU VARSHNEY

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CHAPTER – I

GENERAL INTRODUCTION

A. PESTICIDES

The term pesticide is derived from Latin word *cida* means *"to kill"*. It is defined[1-3] as any substance, preparation or organism used to protect plants, wood or plants products from harmful organisms; to regulate the growth of plants; to give protection against the harmful creatures or to render such creatures harmless. Thus the term pesticide embraces large group of class which includes avicides, chemosterilants, defolints, fungicides, growth regulators, herbicides, insecticides, nematicides, piscicides , repellants, rodenticides, surface biocides and wood preservatives etc.

Pesticides are important component of high – input farming. Therefore, successful large – scale agriculture requires that the vegetation should be free from disease and the land reserved for commercial crop should be free from unwanted growth. Thus pesticides are given a share of credit for the green revolution. Hence, there is a strong tendency in our present civilization to resort to the use of pesticides. On the other hand, usage of pesticides in agriculture has imposed many direct and indirect undesirable effects on the environment. Indiscriminate use of pesticides like DDT, dieldrin and aldrin is of great concern because these chemicals are passed on from one organism to another through all the links of food chain and can ultimately be accumulated in the fat of human body.

Pesticides have high stability, low vapour pressure and very low solubility in water, but have substantial solubility in oils and fats.

For example, the concentration of DDT in fresh water is about 0.00001 ppm. It tends to become more concentrated from a tropical level to another due to the process of biological magnification. As a result of biological magnification fish and predatory birds are very susceptible to chlorinated hydrocarbons like DDT, dieldrin and aldrin. Dieldrin has been found to affect the calcium metabolism in predatory birds and this has resulted in reproductive failure. Thus there is a genuine need of pesticide residues analysis in our ecosystem. Several instrumental[4-10] and non instrumental[11-15] methods have been used for the detection, separation and determination of pesticides in different environmental matrices.

B. CLASSIFICATION OF PESTICIDES

The pesticides have been classified as follows:

1. **Inorganic Pesticides:** About A.D. 70 Pliny the Elder recommended that arsenic could be used to kill insects, and the Chinese used arsenic sulphide as an insecticide as early as the late sixteenth century. Other inorganic products used as pesticides contain antimony, boron, copper, fluorine, manganese, mercury, selenium, sulphur, thallium, tin and zinc as their active ingredients. Although these products are not very effective for pesticidal use, many are so persistent in the soil that there are instances as of crops being damaged by their residues in the soil.

2. **Organic Pesticides:** The era of organic pesticides began from 1940. These chemicals are so successful in controlling the pests that there is extremely rapid and general adoption of them and

development of new ones. This has progressed so rapidly, that today about 1500 pesticides in the form of 10,000 formulations are in common use around the world. Some of the commonly used pesticides are given below:

(a) Carboxylic acid derivatives: TCA, dalapon, 2,4-D, 2,4,5-T etc.

(b) Heterocyclic compounds: benomyl, carboxin, metalaxyl etc.

(c) Organochlorines: aldrin, BHC, DDT, endosulfan, heptachlor etc.

(d) Organonitrogens (Carbamates):baygon, carbaryl, carbofuran, dinocap etc.

(e) Organonitrogen sulphurs (Dithiocarbamates): captafol, captan, folpet etc.

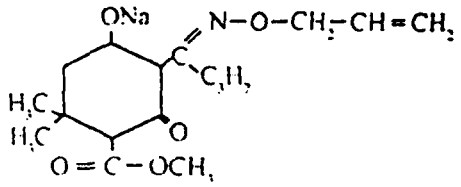
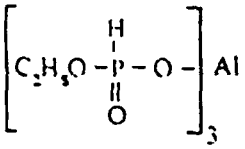
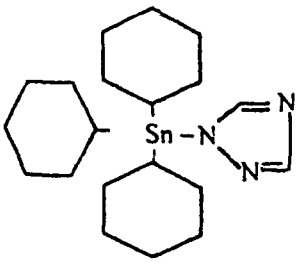
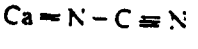
(f) Organophosphates: bromophos, malathion, parathion, phosphamidon etc.

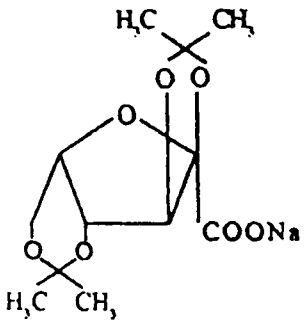
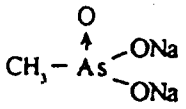
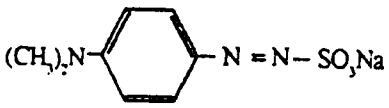
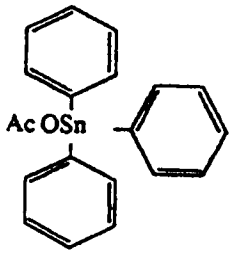
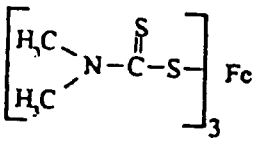
3. **Organic Pesticides Containing Metal Ions**: It is a relatively less familiar class of pesticides. The activity of these pesticides depends on the chelating action of the metal ion as well as the activity of the organic matrix. Some of the organic pesticides containing metal ions (OPCM) are given in Table 1.1.

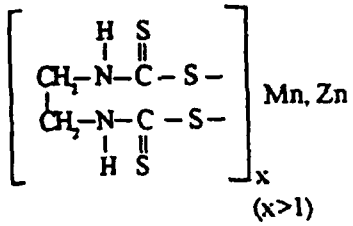
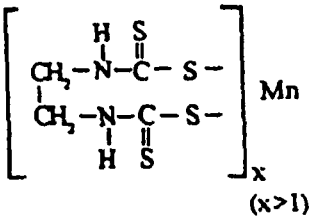
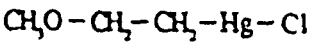
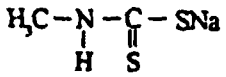
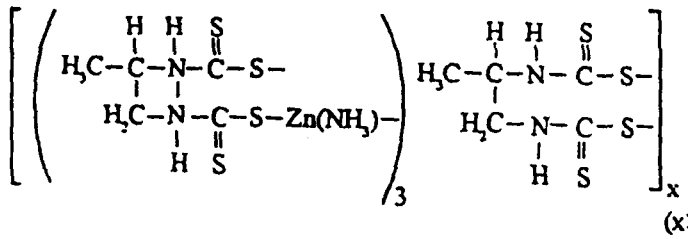
C. APPLICATION OF DITHIOCARBAMATES

1. **Additive in Lubricating Oil:** Tanaka et al.[16,17] have reported a process for producing molybdenum oxysulphide dithiocarbamates as lubricant additives. These dithiocarbamates have been found to be good antifriction and anticorrosive agents in lubricating oil.

Table 1.1: Chemical structure and mode of action of some organic pesticides containing metal ions.

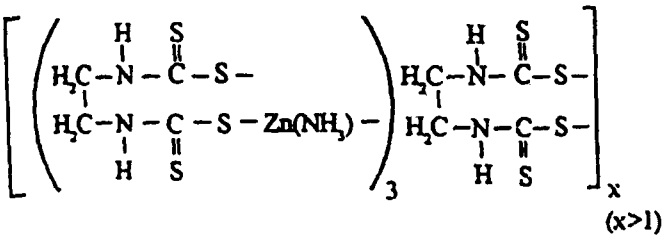
Pesticides	Properties
1. Alloxydim-sodium 	a) Colourless crystals b) 2250 - 2560, > 1630 c) Selective, systemic herbicide
2. Aluminium phosethyl 	a) Colourless crystals b) 5800, > 3200 c) Systemic fungicide
3. Azocyclotin 	a) Colourless crystals b) 99, > 1000 c) Contact acaricide
4. Calcium cyanamide 	a) Grey powder b) 765, - c) Herbicide, fungicide and defoliant

Pesticides	Properties
5. Dikegulac-sodium 	a) Colourless crystals b) 31000, >2000 c) Systemic plant growth regulator
6. Disodium methanearsonate 	a) Colourless crystals b) 1000, - c) Selective post-emergence herbicide
7. Fenaminosulf 	a) Yellow brown crystalline powder b) 60, 100 c) Seed and soil fungicide
8. Fentinacetate 	a) Colourless crystals b) 125-160, 450 c) Non systemic leaf-fungicide, algicide and molluscicide
9. Ferbam 	a) Black powder b) 4000-17000, - c) Protective leaf - fungicide

Pesticides	Properties
10. Mancozeb 	a) Greyish - yellow powder b) 5000, > 10000 c) Protective leaf - fungicide
11. Maneb 	a) Yellow amorphous powder b) 7500, > 5000 c) Protective leaf - fungicide
12. 2-Methoxyethylmercury chloride 	a) Colourless crystals b) 570, - c) Systemic fungicide
13. Metham - sodium 	a) Colourless crystals b) 820, 97 c) Nematicide, fungicide, insecticide and herbicide
14. Methyl - metiram 	a) Pale yellow powder b) 1540, - c) Protective leaf - fungicide and acaricide

Pesticides	Properties

15. Metiram



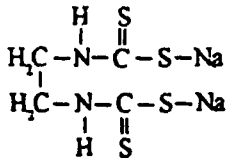
(x>1)

a) Yellow powder

b) 10000, > 2000

c) Protective leaf - fungicide

16. Nabam

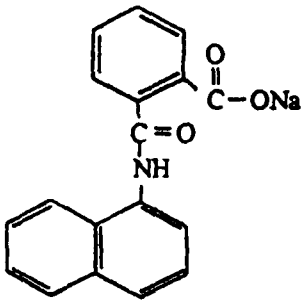


a) Colourless crystals

b) 395, -

c) Protective fungicide and algicide

17. Naptalam

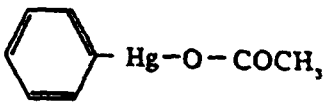


a) White crystals

b) 1900, -

c) Selective pre-emergence herbicide

18. Phenylmercury acetate

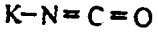


a) Pale yellow powder

b) 50-100, -

c) Eradicative fungicide

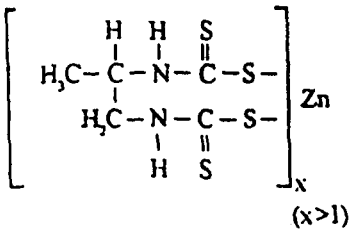
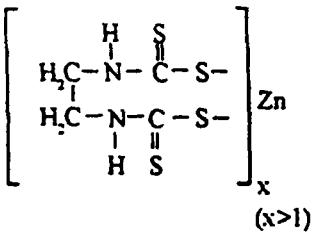
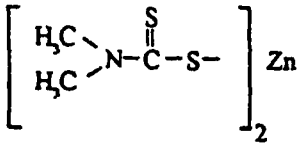
19. Potassium cyanate



a) Colourless crystals

b) 841, -

c) Herbicide

Pesticides	Properties
20. Propineb  (x>1)	a) Pale yellow powder b) 8500, > 1000 c) Protective leaf - fungicide
21. Zineb  (x>1)	a) Light coloured powder b) >5200; > 10000 c) Protective leaf - fungicide
22. Ziram 	a) White powder b) 1400, > 20000 c) Protective leaf - fungicide and repellant

a) Physical appearance
b) Acute oral LD_{50} (rats) and acute dermal LD_{50} (rats) in mg/kg
c) Mode of action

2. **Sulphur Vulcanization:** Niewenhuizen et al.[18] have published a review with 262 references describing methodologies useful in investigating the mechanism of vulcanization and the reactivity of thiuram and dithiocarbamate chemicals.
3. **Graft Copolymerization:** Kim and Cho[19] have synthesized graft copolymers by iniferter-containing macromer. A monomer such as styrene, methylmethacrylate, ethylacrylate or butylacrylate were copolymerised with chloromethylstyrene by AIBN initiation and the chloride group in the polymer was treated with sodium diethyldithiocarbamate to give dithiocarbamate groups . NMR analysis showed that conversion to dithiocarbamate groups was quantitative for acrylate copolymer as well as styrene copolymer.
4. **Chromogenic Reagent:** A spectrophotometric method[20] has been reported for the determination of copper (II) using sodium diethyldithiocarbamate as a colouring reagent. The method is based on the formation of a brown suspension of the copper (II) diethyldithiocarbamate, which can be extracted with butyl acetate, and the coloured extract can be analyzed spectrophotometrically at 430 nm.
5. **Floatation of Non-ferrous Metals:** Glinkin[21] has published a review with 8 refrences describing the floatation of non-ferrous sulphide minerals with dithiocarbamate reagents. It outlines the use of sodium dimethyldithiocarbamate as a deppresor for sphalerite, iron sulphide and S-cyanoethyl-N,N′-diethyldithiocarbamate as a collector for copper and molybdenum sulphides

6. Ion – Exchanger:

a. **Analysis of heavy metal ions:** Airoldi et al.[22] in 1994 have prepared immobilized dithiocarbamate by reacting a 3 – propylethylenediammine group, covalently bonded to silica gel, with carbon disulphide in toluene. The attached dithiocarbamate possess cation-exchange properties in which sodium ion can be exchanged with cobalt, nickel, copper and zinc from ethanolic solution. They have reported that metal: legand ratio of 1:3 for cobalt, 1:2 for nickel and 1:1 for copper and zinc complexes in ethanolic solution. The tentative mechanism is given in scheme no.1.

Tang et al.[23] in 1998 have prepared a new ion-exchange chelating fiber with aminophosphonic and dithiocarbamate groups. based on polyacrylonitrile for the simultaneous preconcentration of beryllium, bismuth, cobalt, gallium, silver, lead, cadmium, copper, manganese and indium in sea water. The fiber capacity was found to be 74.1, 59.2, 69.2,31.9, 4.05, 9.57, 0.834, 3.06, 27.6, 3.06 μ mol g^{-1} for Be, Mn, Co, Cu, Ga, Ag, Cd, In, Pb, Bi respectively at pH 6.The sample flow rate and eluent flow rate were found to be 5 ml min^{-1} and 1 ml min^{-1} respectively. It has been claimed that the metal ion can be concentrated to 200 times and the technique can be coupled with inductively coupled argon plasma – mass spectroscopy (ICP – MS) to provide a promising method for the determination of trace elements in sea water.

Hamilton and Fulton[24] have carried out the removal of mercury from wastewater using new selective adsorbent

material. This adsorbent material is a porous resin having immobilized mercury selective chelating groups bound thereto. A particularly preferred adsorbent material is a cross linked styrene – divinylbenzene copolymer having immobilized dithiocarbamate groups bound thereto. Mercury containing wastewater containing mercury-complexing material comprising treating waste water containing mercury ions with strong oxidizing agent in a reaction chamber to produce pretreated wastewater by removing an effluent stream of pretreated wastewater from the reaction chamber and passing effluent stream of pretreated wastewater through a column packed with a mercury – selective adsorbent material to produce an effluent stream of wastewater having a reduced mercury content.

Tandon et al.[25] have studied N–benzyl–D–glucaminedithiocarbamate and its analog N–(4– methoxybenzyl –D–glucaminedithiocarbamate) which are effective chelators of cadmium for their efficacy to induce excretion of lead to reduce tissue burden of lead in pre – exposed rats. These dithiocarbamates have been found to be effective in reducing hepatic and renal lead levels but not of brain lead levels.

b. **Solubility of dithiocarbamates:** The literature survey[26] shows that the dithiocarbamic acids are unstable and their sodium and ammonium salts are stable. The dithiocarbamates of metal of atomic number more than 20 are insoluble in water as well as in organic solvents. Some anhydrous dithiocarbamates are soluble in organic solvents.

(i) Water insoluble dithiocarbamates can be dissolved in aqueous medium in presence of versenate (EDTA), ammonium hydroxide – ammonium chloride buffer solution of pH 10. Hence it is clear that when zineb, Zinc ethylene bis(dithiocarbamate) is treated with 1 M solution of EDTA in presence of ammonium buffer of pH 10, it converts to water soluble complex such as ammonium salt of ethylene bis (dithiocarbamate) and zinc form of ethylenediamine tetraacetic acid (EDTA). The tentative mechanism is given in scheme no.2.

Similarly a water soluble complex of sodium ethylene bis (dithiocarbamate) and precipitate of zinc hydroxide are obtained when zinc ethylene bis (dithiocarbamate) (zineb) is treated wih 0.1 M solution of sodium hydroxide.

(ii) Insoluble dithicarbamates can also be dissolved in presence of cation – exchange resin either in Na^+ or NH_4^+ forms. Hence it is clear that Zn^{2+} is exchanged by Na^+ to give water soluble sodium salt of ethylene bis(dithiocarbamate). The tentative mechanism is given in scheme no.3.

7. Synthesis of New Compounds:

a. **Sulfines:** Cherrie and Metzner [27] have demonstrated that the oxidation reaction of various dithiocarbamates gives corresponding sulfines (S-oxides). The sulfines decomposed to thiocarbamates and dithiocarbamates on keeping them at ambient temperature.

b. **Drugs:** Ching [28] has proposed a new method of synthesis of conjugates of nitric oxide scavengers (e.g. dithiocarbamates) with drugs (e.g. NSAIDS). These conjugates provide a new

class of drugs (e:g anti-inflammatory agents) and they have much lower incidence of side effects and are more effective than unmodified drugs because cells and tissues contacted by them are protected from the potentially damaging effects of nitric oxide over production.

D. CARBAMATES RESIDUES ANALYSIS:

1. **Spot Test:** Spot tests are simple, sensitive, selective or specific, inexpensive and rapid. The spot test analysis has been found to be extremely useful for the preliminary on-field detection of pesticides. Generally, a preliminary examination of a test material is required before undertaking costly and sophisticated quantitative analysis in order to minimize time and operation costs. Recently, the following tests have been developed for the detection and semi-quantitative determination of pesticide residues in environmental samples.

A Paper spot test has been developed[29] for the detection of carbaryl in water. To carry out this test a paper strip impregnated with sodium hydroxide was spotted with carbaryl and then it was treated with 2, 6 – dichloroquinone – 4 – chloroimine. A violet spot appears if carbaryl is present. The lower limit of detection is found to be 0.06 μg / spot. The tentative mechanism is given in scheme no.4.

Padilkar et al.[30] have reported a thin layer chromatography spot test for the determination of carbaryl. Slica gel G coated thin layer chromatography (TLC) plates spotted with carbaryl gives violet colour on treating with copper (II) chloride solution followed

by ammonium metavandate reagent. The lower limits of detection for carbaryl and 1–naphthol are 10 μg / spot and 1 μg / spot respectively. The lower limit of detection is 1 μg / spot for carbaryl and 1–naphthol both when alkaline hexacyanoferrate (III) is used as a chromogenic reagent. Other insecticides such as malathion, parathion, dimethoate, sumithion, ekalax, eldrin, DDT, baygon, carbofuran and zineb do not interfere. The tentative mechanism is given in scheme no.5. A selective, sensitive, simple and inexpensive spot test is described[31] for the detection of mancozeb at trace levels in the soil, vegetation and water. It is based upon the intensive catalytic action of dithiocarbamates on the production of nitrogen from sodium azide reaction with iodine. The chemical reactions involved are given in scheme no.6. A spot test has been developed for the on-field detection of dithiocarbamates fungicides[32] at μg levels in soil, vegetation and water. Copper – ammonia complex on cation – exchange resin beads in presence of diethanolamine has been used as a chromogenic reagent for carbon disulphide.The reaction involved has been shown in scheme no.7. A spot test has been developed[33] using sulphanilic acid – sodium nitrite – sodium hydroxide, 8 – hydroquinoline and alkaline hexacyanoferrate (III) as colouring reagents for the sensitive and selective detection of carbaryl at μg level in environmental samples. The tentative reaction mechanism is shown in scheme no. 8. A already known, spot test for dithiocarbamates[33], is extended for the selective detection of mancozeb at μg levels in

its formulations and water. Copper (II) chloride – acetic acid is used as a colouring reagent. The reaction mechanism is shown in scheme no. 9. A colour reaction based[34] on the formation of black lead sulfide by treatment of mancozeb with alkaline plumbite solution has been developed for the thin layer chromatography (TLC) detection of mancozeb.The lower limit of detection on a silica gel plate is 0.45 μg / spot. Fungicides other than dithiocarbamates do not interfere with the test. The test can also be applied for the detection of mancozeb in soil extracts. A tentative reaction mechanism is shown in scheme no. 10.

2. **Spectroscopic and Spectrophotometric Methods:** These methods are simple, direct, sensitive and rapid but they do not achieve the sensitivity of thin layer chromatography and gas chromatography techniques. They may not be able to distinguish between the parent compound, and its metabolites and hydrolysis products but they can be used with chromatography as a confirmatory technique. Spectrophotometry is a reliable and routinely used technique that is readily available for analysts. A few papers have been reported in this area.

Cullen[35] has carried out spectrophotometric determination of zineb, maneb, ziram, ferbam, thiram and metiram residues on food crops. The residues were decomposed on the crop and the evolved carbon disulphide was collected and reacted with cupric acetate – diethanolamine in ethanol (0.0016%) to form the yellow cupric salt of N, N/ bis (2 – hydroxyethyl) dithiocarbamic acid which can be measured

colourimetrically at 435 nm. The speed of decomposition of the dithiocarbamate and the copper – carbon disulphide ratio were found to be critical factors. This method is sensitive to 20 μg of carbon disulphide.

Caldas et al.[36] has also carried out a method of determination of dithiocarbamate residues in food spectrophotometrically using a vertical disulphide reaction system. In this reaction system the CS_2 formed by acid hydrolysis of the dithiocarbamates passes through 10 % NaOH solution and then the gas passed through a solution of copper (II) acetate monohydrate (colour reagent) which has been analysed spectrophotometrically at 435 nm.

Malik[37] has developed a procedure for the determination of ziram, zineb and ferbam dithiocarbamate pesticides by converting ziram and zineb into zinc – phenylfluorone complex and ferbam into an iron phenylfluorone complex which are then dissolved in water in the presence of cetylpyridinium bromide and pyridene as a surfactant and analyzed spectrophotometrically.

Rao and Malik[38] have developed a method for the determination of zinc (II) dimethyldithiocarbamate (ziram) by converting it into copper (II) dithiocarbamate complex, which is then extracted into molten naphthalene. The absorbance is measured at 430 nm versus a reagent blank.

Rao et al.[39] have developed a new, rapid, sensitive and selective method for the determination of ziram and zineb dithiocarbamate. The method is based on the formation of zinc – thiazolyazo – 2 – naphthol (Zn – TAN) complex which is insoluble

in water but is solublized by adding octylphenolpoly(ethylene glycol) ether ie.Triton X – 100 which acts as a solubilizing and sensitizing agent. The formed violet coloured complex is analyzed spectrophotometrically at 580 nm.

3. **Volumetric Method:** A simple, inexpensive and rapid complexometric titration[40] has been developed for the determination of mancozeb.The procedure is based on the fact that mancozeb dissolves (at ppm level) in ammonia buffer of pH 10 in presence of versenate solution. The quantification is made on the basis of versenate consumed in the process of dissolution. The end point was detected by using visual indicator, Eriochrome BlackT, which gives wine red colour with zinc (II) and manganese (II) and changes to sky blue at the end point on titrating with versenate solution at pH 10.

   A simple and sensitive complexometric titration[41] has been developed for the determination of sodium diethyldithiocarbamate. The method is based on the fact that carbon disulphide formed by acid decomposition is passed through 10% lead acetate and then through 2N methanolic KOH solution forming potassium ethylxanthogenate. After neutralization of this solution by adding phenolphthalein and 30% acetic acid, it was titrated with iodine solution using starch solution as indicator.

4. **Atomic Absorption Spectrophotometric Methods:** Rathore et al.[42] have carried out atomic absorption spectrophotometric determination of mancozeb residues, micronutrients (Mn^{2+} and Zn^{2+}) in plants. It is based on the decomposition of organic matrix

by treating mancozeb with oxidizing mixture (nitric acid – perchloric acid) and the determination of zinc or manganese in the residue by using atomic absorption spectrophotometer. The lower limit of determination has been reported to be at ppm level. The results of atomic absorption spectrophotometry have been compared with those obtaind by volumetry in which disodium salt of ethylene diamminetetraacetic acid, Eriochrome Black T and ammonia buffer of pH 10 have been used.

5. Chromatographic Methods:

a) **High performance liquid chromatography**: Zhou et al.[43] have established a derivative high performance liquid chromatography method for quantitative determination of cisplatin in emulsions. Cisplatin was extracted by dimethylsulphoxide (DMSO) from emulsions and reacted with sodium diethyldithiocarbamate (NaDDC) to produce a Pt $(DDC)_2$ complex, which was extracted by chloroform and detected at 254 nm. An analytical column, U- Bondapak – $C_{18}H_{37}$ (5 μm, 150mm x 4m) was used with MeOH – H_2O (80:20) as the mobile phase at a flow rate of 1ml/min. Nickel chloride was used as an internal standard. The main recovery of extraction has been found to be 78.4% with relative standard deviation < 5%.

b) **Gas chromatography:** Woodrow et al.[44] have trapped air borne particulate residues that resulted from commercial applications of the dithiocarbamate fungicides (ziram and mancozeb) on glass fiber filters at 14 – 16 l/min upto 24 hrs. Hydrochloric acid hydrolysis, with stannous chloride reduction, is used to convert

these residues to carbon disulphide, which is partitioned into isooctane for assay using sulphur mode flame photometric gas chromatography. Limits of detection have been found to be about 0.3 μg (ziram) and 0.5 μg (mancozeb) per filter, which are equivalent to about 14 – 23 ng /m^3 (24hrs).

c) **Thin layer chromatography :** It has been reported that the admixtures of heavy metal[45] ions such as Mn^{2+}, Fe^{3+},Co^{2+},Ni^{2+},Cu^{2+},Bi^{3+} and Ag^{+} can be separated on cellulose plates impregnated with sodium diethyldithiocarbamate using organic solvents as mobile phase.

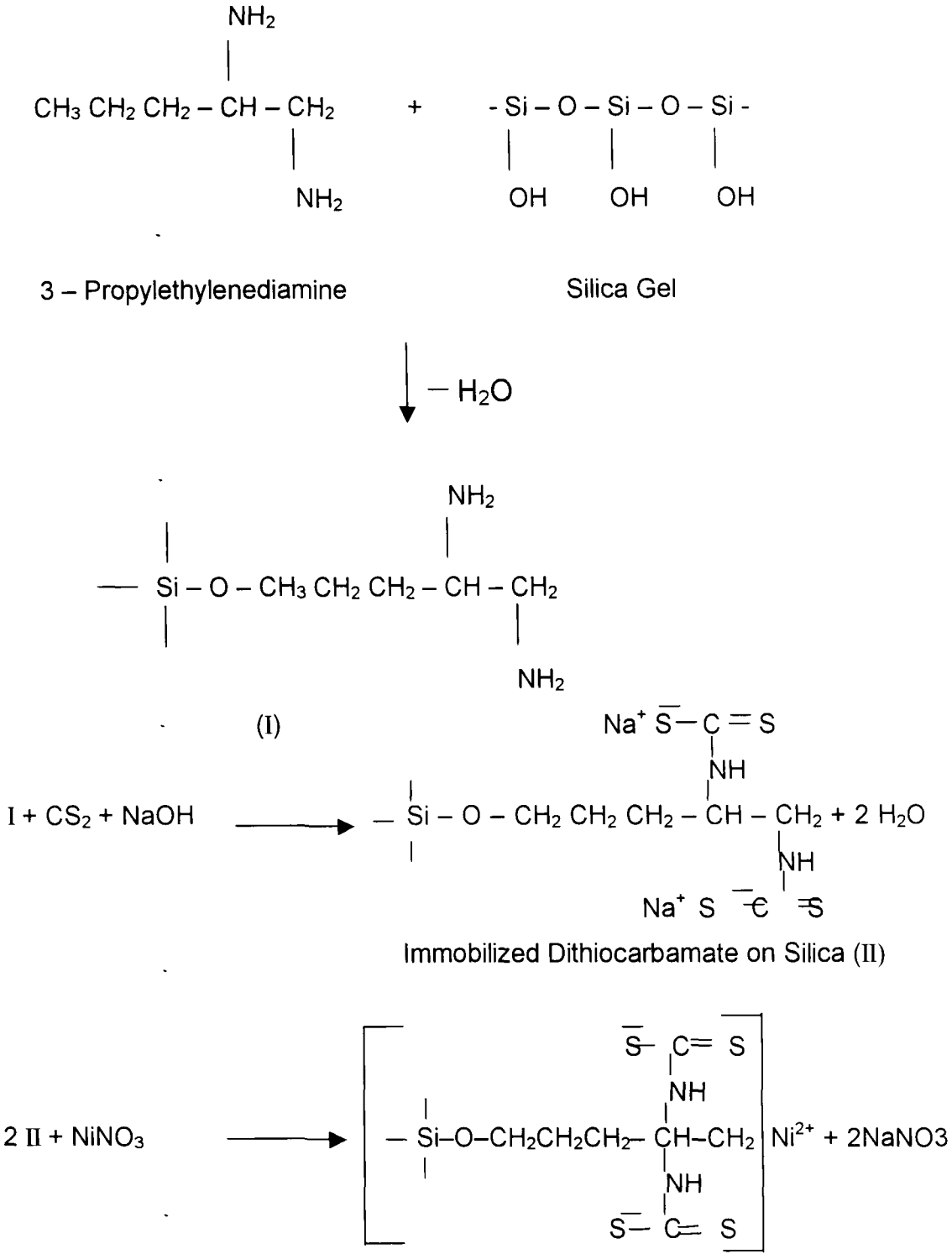
d) **Paper chromatography :** Rathore and Kumar[46] have performed chromatography of Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Hg^{+} and Pb^{2+} on paper strips impregnated with sodium diethyl dithiocarbamate and its admixtures with SiO_2,$CaSO_4$, Na_2CO_3, NaCl, NH_4Cl, EDTA, NaOH, $CaCO_3$, Na_2HPO_4 and H_3PO_4. Several binary separations have been achieved experimentally.

E. WORK DONE

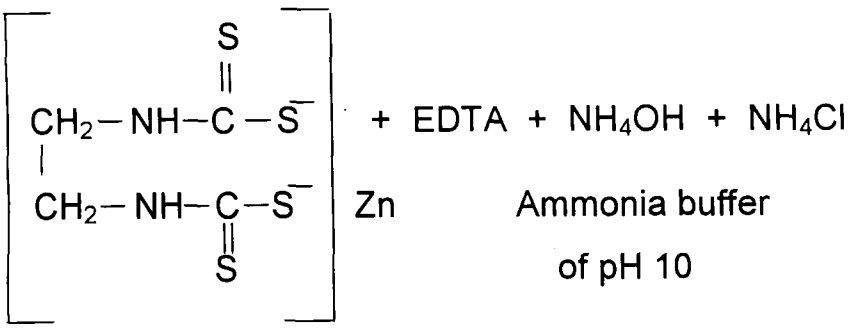
The following procedure has been developed for the Spectrophotometric determination of sodium diethyldithiocarbamate and zinc dimethyldithiocarbamate in water and cereal:

Aqueous solutions of copper sulphate pentahydrate (10 ml of 0.20%) and citric acid (5 ml of 25%) were taken in a conical flask. The mixture was rendered slightly alkaline with dilute

ammonia solution. The excess ammonia was boiled off and then EDTA (15 ml of 4.0%) was added into it. The reaction mixture was cooled to room temperature (25°C) and transferred into a separatory funnel. A known volume of NaDDC solution or ziram suspension was added into it. The mixture was shaken for 45 sec and the yellow product was extracted in 10 ml of n-butyl acetate. The absorbance of the extract was recorded at 430nm.The results obtained are described in this dissertation.

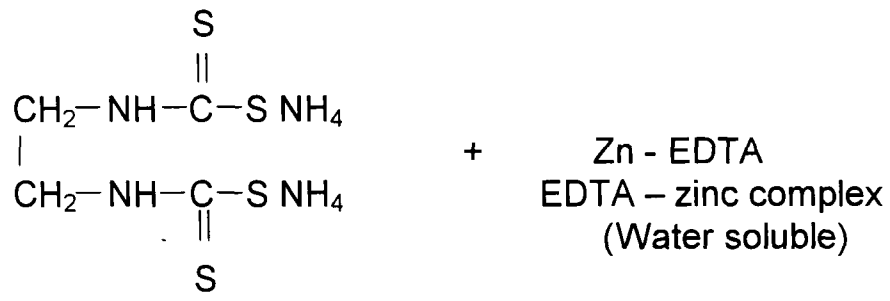


Scheme 1: Reaction of immobilized dithiocarbamate with metal ion solution



Zinc ethylenebis (dithiocarbamate)

(Water insoluble)

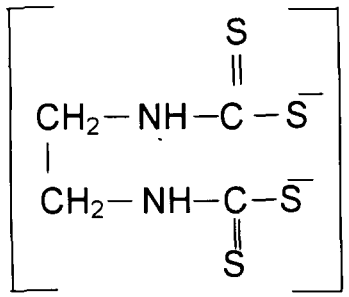


Ammonium salt of

zinc ethylenebis (dithiocarbamate)

(Water-soluble)

Scheme 2: Conversion of insoluble dithiocarbamate into soluble dithiocarbamate by ion-exchange reaction with EDTA and ammonia buffer

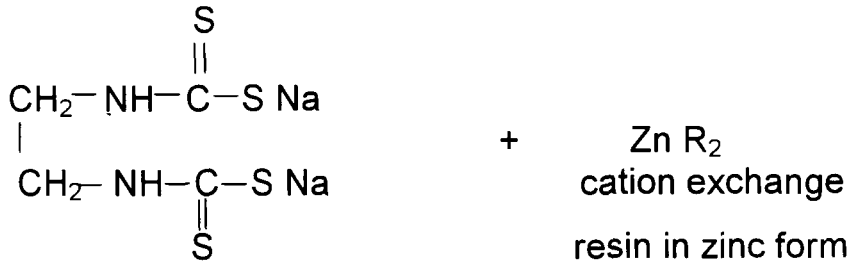


Zinc ethylenebis (dithiocarbamate)

(Water insoluble)

+ 2 NaR

Cation exchange resin in sodium form



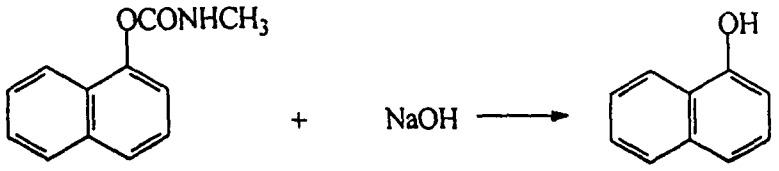
Sodium salt of ethylenebis(dithiocarbamate)

(Water soluble)

+ $Zn\ R_2$

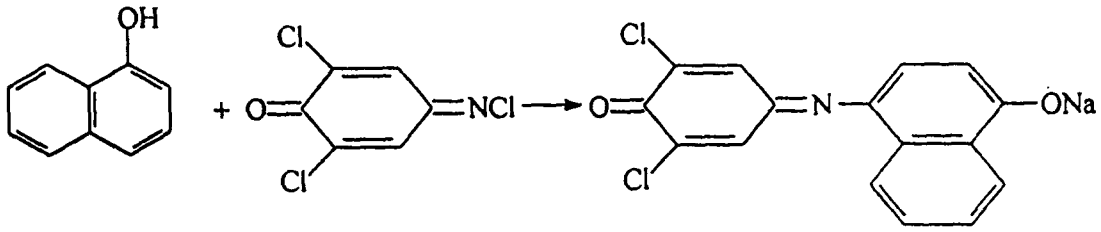
cation exchange resin in zinc form

Scheme 3: Conversion of insoluble dithiocarbamate into soluble dithiocarbamate by ion-exchange reaction with cation ion exchange resin.



Carbaryl

1-naphthol

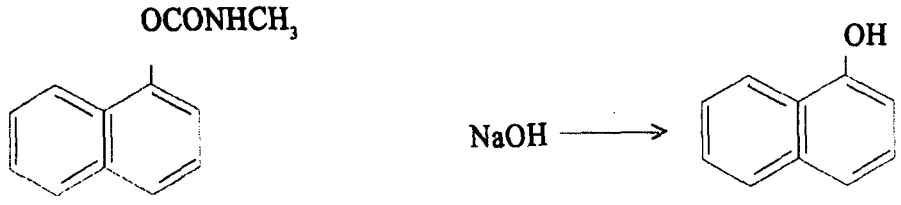


1-naphthol

2,6-dichloroquinone-4-chloroimine

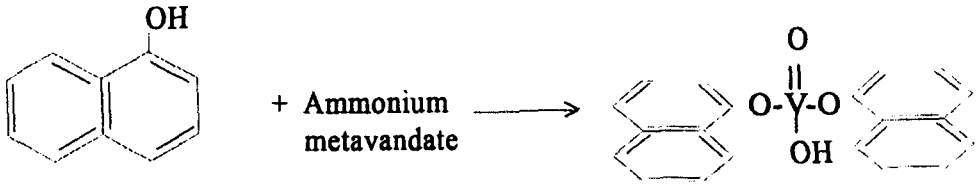
Indonaphthol dye (Blue)

Scheme4 :Colour reaction of carbaryl with 2,6-dichloroquinone-4-chloroimine



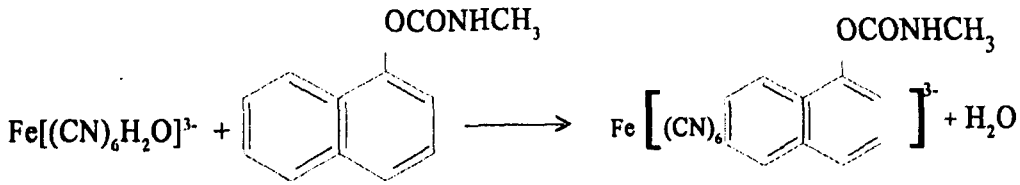
Carbaryl

1- naphthol



1- naphthol

Violet Complex

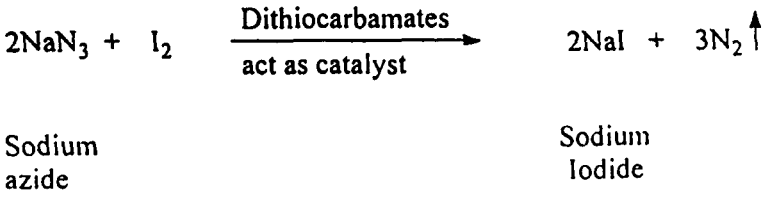


Alkaline hexacyanoferrate

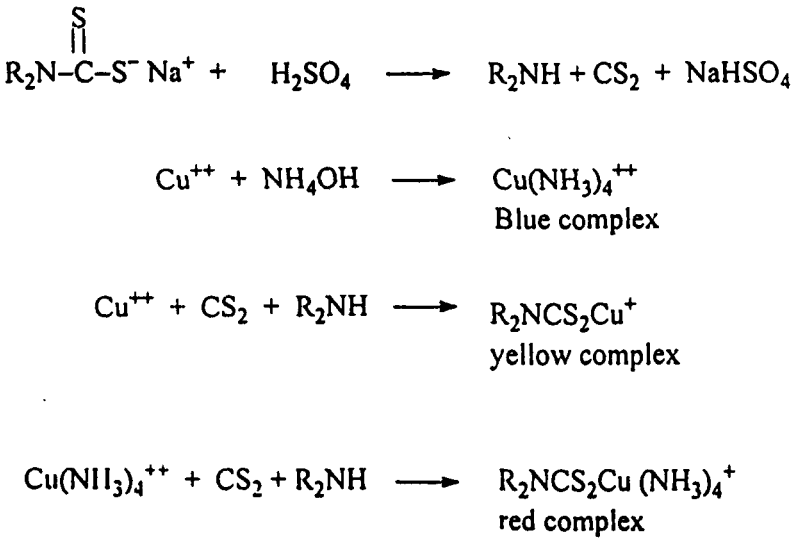
Carbaryl

Carbaryl hexacyanoferrate (Violet Colour)

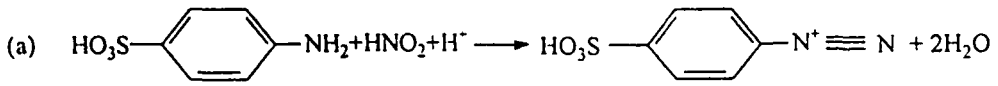
Scheme 5: Colour recation of carbaryl with ammonium metavandate and hexacyanoferrate



Scheme 6: Vigorous evolution of bubbles of nitrogen by using dithiocarbamate as a catalyst.

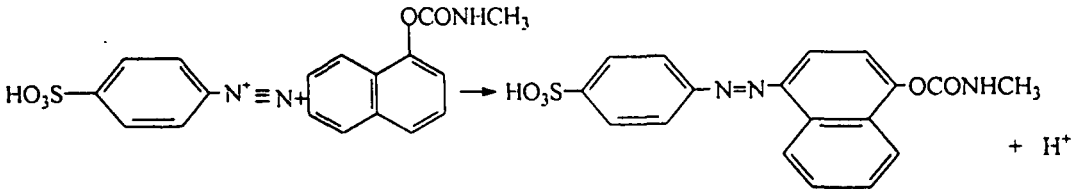


Scheme 7: Colour reaction of copper-ammonia complex with dithiocarbamate.



Sulphanilic acid

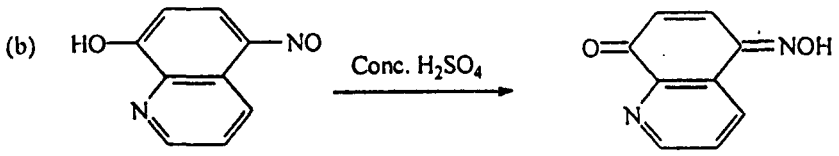
Diazobenzene Sulphonic acid



Diazobenzene Sulphonic acid

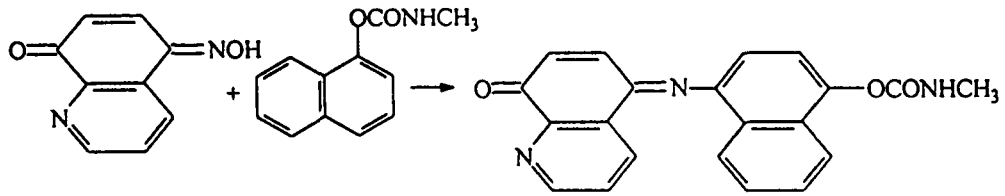
Carbaryl

Dye stuffs (Pink colour)



5-nitroso-8-hydroxyquinoline

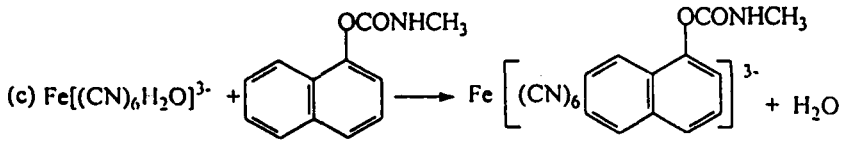
Oxime



Oxime

Carbaryl

Brown colour

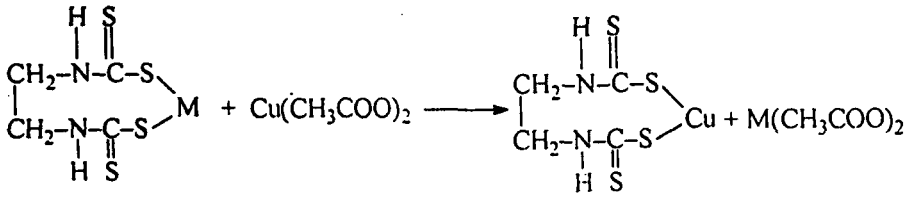


Alkaline hexacyanoferrate

Carbaryl

Carbaryl hexacyanoferrate (Violet colour)

Scheme 8: Colour reaction of carbaryl with (a) sulphanilic acid in the presence of sodium nitrite (b) 5-nitroso-8-hydroxyquinoline (c) alkaline hexacyanoferrate (III).

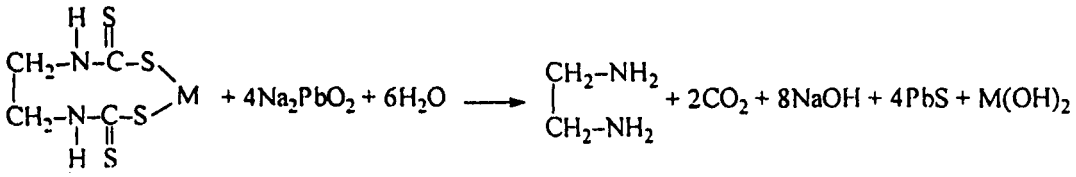


Yellow salt

Yellow brown colour

Where M=Zn^{+2} or Mn^{+2}

Scheme 9: Colour reaction of mancozeb with copper acetate



Yellow salt

Yellow brown colour

Black ppt

Where M=Zn^{+2} or Mn^{+2}

Scheme 10: Colour reaction of mancozeb with lead plumbite

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CHAPTER – II

Simple and Selective Spectrophotometric Method for the Routine Determination of Ziram Residues using Ion-Exchange Dissolution

A. INTRODUCTION

Dithiocarbamates are being used as fungicide[1-6], ion exchanger[7], chromogenic reagent[8].These are also being used in lubricating oil[9,10], sulphur vulcanization[11], graft copolymerization[12], floatation of non – ferrous metals[13], as etc. The concentration of dithiocarbamates is increasing day by day in the environment due to their repetitive and continuous use in crop protection and storage of foodstuffs. Amongst different analytical methods, spectrophotometry has been found to be simple and inexpensive for the routine and accurate analysis of dithiocarbamates in foodstuffs[14].Therefore, a known spectrophotometric method previously used for the determination of Cu (II) has been now extended for the determination of sodium diethyldithiocarbamate (NaDDC) and zinc dimethyldithiocarbamate (ziram) in water, food grains and formulations. The results obtained are described in this chapter.

B. EXPERIMENTAL

1. **Apparatus**: A visible spectrophotometer CL 24 (Elico, India) was used.
2. **Reagent:** Sodium diethyldithiocarbamate (NaDDC), copper sulphate pentahydrate and n–butyl acetate; zinc dimethyldithiocarbamate (ziram formulation); mancozeb (WP); and carbon disulphide (CS_2) were LR grade chemicals from CDH; GSC; MIL; and SDFC respectively. All other reagents

were used of analytical grade. Ziram synthesized in our laboratory was used as a standard material.

3. **Preparation of Solutions:** Solutions of NaDDC (0.01%), copper sulphate pentahydrate (0.20%), citric acid (25%), dimethylamine (25 – 30% w/v), sodium hydroxide (80%), zinc sulphate (0.10 N) and disodium salt of ethylenediamine tetraacetic acid (EDTA) (4.0%) were prepared in distilled water (DW). Suspensions of ziram (1.0%), ziram formulation (1.0%) and mancozeb (1.0%) were prepared in DW.

4. **Composition of Tap Water:** The tap water was composed of 91 ppm total alkalinity as $CaCO_3$, 203 ppm total hardness as $CaCO_3$; 13-14 ppm chloride; 14-18.5 ppm sulphate; 0.99-1.0 ppm fluoride; 2.1-2.5 ppm nitrate-nitrogen; 1.25-1.50 ppm cadmium; 4.5-5.0 ppm copper; 2.0-2.5 ppm chromium; 15-16 ppm manganese; 8.5-10 ppm nickel; 0.70-0.80 ppm lead; 132-139 ppm zinc; 132.25-134.56 μ ohm^{-1} elecrical conductivity and pH 8.

5. **Synthesis of Ziram:** Dimethylamine (18 ml of 25 – 30 % w/v) was taken in a conical flask, cooled in ice bath at 3 – 5^0C and sodium hydroxide solution (5 ml of 80%) was added to it with constant stirring .CS_2 (6 ml) was added drop wise to this mixture making sure that no fumes escape from flask. The reaction mixture was stirred for 4h at 10°C and kept over a night in refrigerator. The needle shaped crystals separated out. The crystals were dissolved in DW and then zinc sulphate (100 ml of 0.10 N) was added into it with constant stirring for 2h. The microcrystalline solid so obtained was filtered, washed with DW

(2 X 20 ml), dried at room temperature (30°C) and desiccated on calcium oxide. The purity of the product was tested by measuring melting point (246°C) and by TLC analysis in chloroform and carbon disulphide.

6. **Development of Colour:** Aqueous solutions of copper sulphate pentahydrate (10 ml of 0.20%) and citric acid (5 ml of 25%) were taken in a conical flask. The mixture was rendered slightly alkaline with dilute ammonia solution. The excess ammonia was boiled off and then EDTA (15 ml of 4.0%) was added into it. The reaction mixture was cooled to room temperature (25°C) and transferred into a separatory funnel. A known volume of NaDDC solution or ziram suspension was added into it. The mixture was shaken for 45 sec and the yellow product was extracted in 10 ml of n-butyl acetate.
7. **The Absorption Spectra:** The absorbance of above yellow extract was recorded at different wavelengths using the reagent blank. The results obtained are shown in Fig.1.
8. **Effect of Temperature:** the reaction mixture was kept at 0°C, 5°C, 35°C and 45°C for 10min. Then the coloured product was extracted in n-butyl acetate at room temperature (25°C). The absorbance was recorded at λ_{max} (430nm) against the reagent blank. The results obtained are shown in Fig.2.
9. **Effect of Time:** The yellow extract was placed at room temperature (25°C) and the absorbance was recorded with different periods of time against the reagent blank. The results obtained are shown in Fig.3.

10. **Calibration Curve:** Calibration curve were made by taking the solutions of different concentration in different conical flasks. The reagents were added into it and the colour was developed by using the above mentioned procedure. The absorbance of the yellow extract was recorded against the reagent blank at 430nm.The Beer–Lambert's law is followed from 1 to 10µg ml^{-1} and 5 to 40µg ml^{-1} for NaDDC and ziram respectively. The curves obtained are shown in fig.4.

11. **Effect of Foreign Substances:** The effect of the foreign substances on the absorbance was studied by adding the following in the reaction mixture. The limit of tolerance of the substances is given in the paranthesis: aqueous solution of zinc sulphate (0.05-0.5mg), manganese sulphate (0.1- 1.0 mg), ferrous sulphate (0.05-0.5 mg), ferric chloride (0.05-0.5mg), nickel chloride (0.05-0.5 mg) and lead sulphate (0.05-0.5 mg) and aqueous suspension of mancozeb (0.1-1.0 mg), benzene hexachloride (BHC) (0.1-1.0 mg) and malathion (0.1-1.0 mg). The colour was developed, extracted and the absorbance was recorded at 430nm. The results obtained are given in Table 1.

12. **Determination of Ziram Residues in Tap Water:** Ziram (5-20 µg ml^{-1}) was extracted from dosed tap water (100 ml) with 5 ml of chloroform. The chloroform was removed and the residue was treated with the reagent to develop the colour. The colour was extracted and the absorbance was recorded. The samples of water were also extracted with 2 X 5 ml of chloroform and 3 X 5 ml of chloroform in order to improve the recovery and then

the above procedure was applied. The results obtained are given in Table 2.

13. **Determination of Ziram Residues in Grains:** The suspension of ziram (5 - 20 μg ml^{-1}) in DW was dosed in wheat (5 gm), arhar pulse (5 gm) and groundnut seeds (5 gm). The dosed grains samples were kept at room temperature (25^0C) for 24h and ziram residues were extracted with 5 ml of chloroform. The solvent was removed and the residue was treated with the reagent in order to develop the colour. The colour was extracted with n-butyl acetate and the absorbance was recorded at 430 nm. The results obtained are given in Table 3.
14. **Determination of Ziram Residues in Formulations:** Ziram (5-40μgml^{-1}) was determined in aqueous suspension of ziram formulation by using the aforesaid spectrophotometric procedure. The results obtained are given in Table 4.

C. CALCULATION

The standard deviation (s), coefficient of variation (C.V), average deviation ($\bar{d}$) and molar absorptivity (ε) were calculated from the following expression:

$$S = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}}$$

$$C.V = \frac{S}{\bar{X}} \times 100$$

$$\bar{d} = \frac{\sum (x - \bar{x})}{n}$$

$$\varepsilon = \frac{AM}{bC}$$

x = Value measured

$\bar{x}$ = Arithmetic mean of x

n = Number of value measured

A = Absorbance

M = Molecular weight

b = Path length = 1 cm

C = Concentration in gm/l

The results obtained are given in Table 5.

D. **RESULT AND DISCUSSION:** The literature survey shows that the following procedures have been used for the routine analysis of metal dithiocarbamate fungicides residues analysis:

1. The standard carbon disulphide evolution method – Cullen[15] has revised it for determining dithiocarbamates residues on food crops i.e.; the residue is decomposed on the crop, the evolved carbon disulphides collected and reacted to form the yellow cupric salt of N, N-bis(2-hydroxyethyl) dithiocarbamic acid which has been measured spectrophotometrically (Table 6). It is sophisticated method as an intensive care is required for the total decomposing of dithiocarbamate and then the conversion of carbon disulphide

into a coloured product. The precision of the method is affected by many variables, the most important of which, is sampling techniques. However, the technique is well versatile, so it has been used for spectrophotometric determination of numerous[15] compounds, which can produce carbon disulphide.

2a. The reaction of metal part of fungicide molecule with chromogenic reagents- Rao[16] et al have developed spectrophotometric determination of ziram and zineb in formulations, crops and synthetic mixture (Table 6). It is based on the formation of zinc-thiazolylazo –2-naphthol complex, which is insoluble in water, but it is solublized by adding triton X – 100, which acts as a solublizing and sensitizing agent.

2b. Determination of metal part – Rathore[17] et al. have determined mancozeb residues in edible plants and vegetables. The sample was crushed, powered and dissolved in sulphuric acid (Table 6). The organic matter was removed by oxidation and then metal concentration was determined either by EDTA titration or by atomic absorption spectrophotometer. The EDTA method has been claimed to be a simple, inexpensive and readily available tool for determining the change in the heavy metal ion concentration in plants due to the use of metal containing fungicides such as mancozeb.

3. Conversion of colourless dithiocarbamate into a colored dithiocarbamate – Malik and Rao[18] have developed (Table 6) a spectrophotometric method for the determination of zinc (II) dithiocarbamate by converting it into coloured Cu (II) dithiocarbamate complex and extracted into molten naphthalene.

The absorbance is measured at 430 nm versus a reagent blank. It is a sensitive method and can be applied for the determination of ziram in formulations and wheat grains.

In this paper efforts have been made to extend a known spectrophotometric method (previously used for the determination of Cu (II)) for the determination of some dithiocarbamates.Fig.2 shows that the reaction is more sensitive at 25°C. Fig.3 shows that the coloured product in butyl acetate is stable for 1½ h at 25°C. The aqueous solution of sodium diethyldithiocarbamate gives coloured product immediately while the suspension of ziram requires a thorough shaking at least for 1 min. to produce the colored product. It is due to the conversion of water insoluble zinc dimethyldithiocarbamate to water soluble ammonium dimethyldithiocarbamate as by ion – exchange process. Zinc ions react with EDTA to make water soluble zinc- EDTA complex. Aqueous suspension of mancozeb does not produce any colour. It is clear from Table 1 that the common substances such as zinc sulphate, magnese sulphate,ferrous sulphate, ferric chloride, nickel chloride, lead sulphate, mancozeb, BHC and malathion do not interfere in this method. The method has appreciable limit of tolerance for chloropesticides such as BHC (0.1-1.0 mg), phosphorous pesticides such as malathion (0.1-1.0 mg) and sulphur pesticides such as mancozeb (0.1-1.0 mg). The results summarized in Tables 2, 3 and 4 shows that this method might be used for the determination of ziram residues in cereals, water and formulations. It is also clear that the recovery is poor in pulses and

grains of groundnut. It may be due to irreversible absorption of ziram on pulses and grains of groundnut.

E. CONCLUSION: The method under study is simple, inexpensive, selective and rapid. It can be used for routine analysis of ziram residue in formulations, water and cereals.

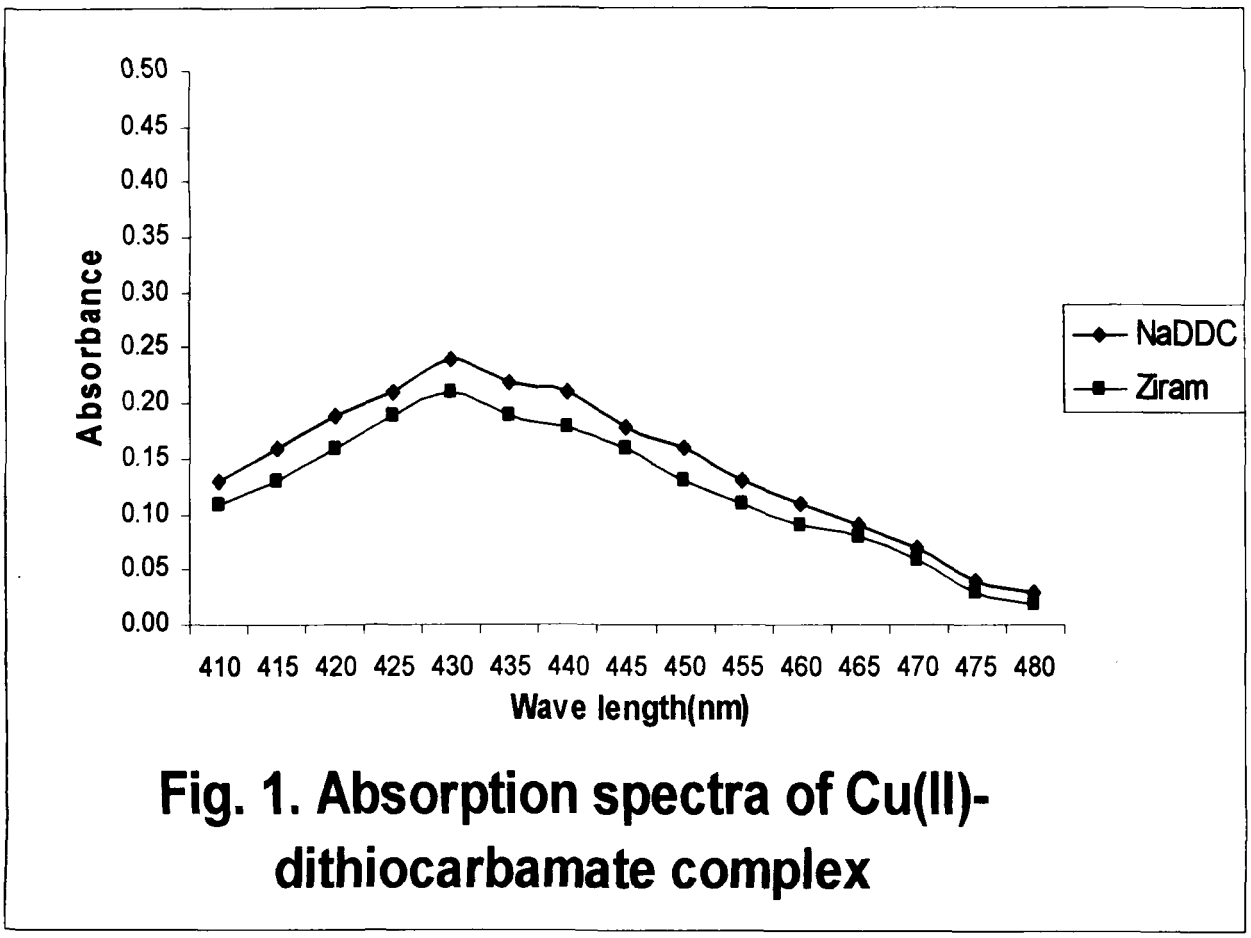

Fig. 1. Absorption spectra of Cu(II)-dithiocarbamate complex

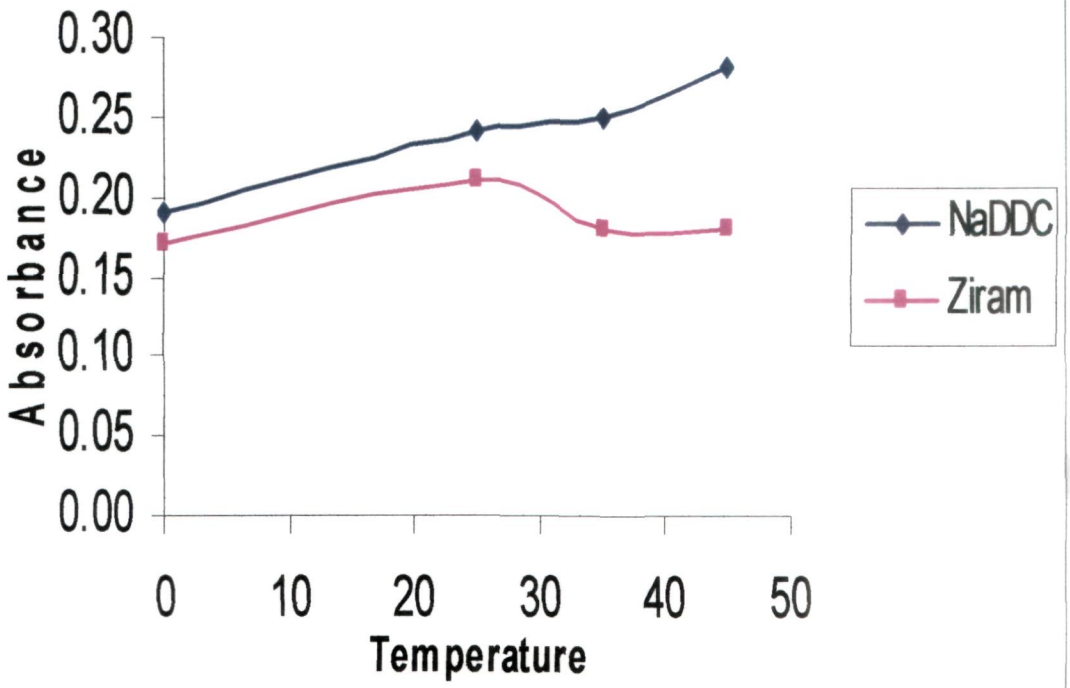

Fig 2. Effect of temperature on absorbance of Cu(II) - dithiocarbamate complex

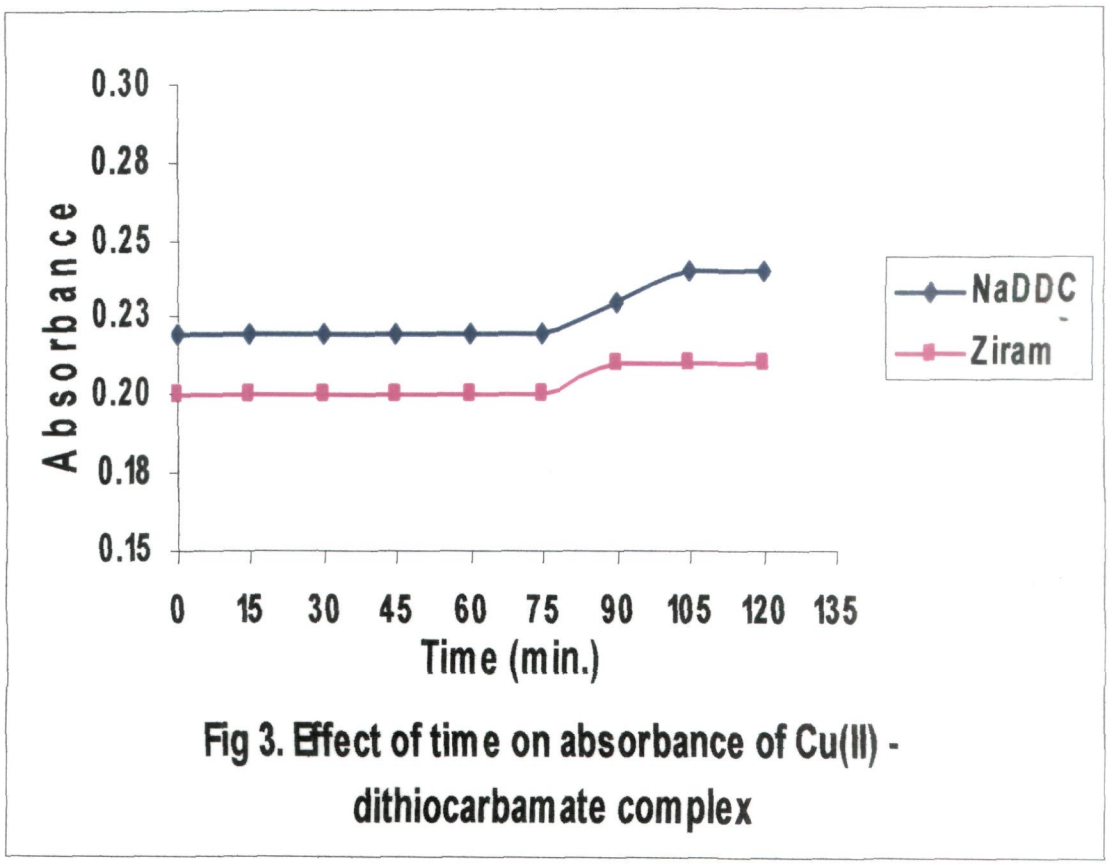

Fig 3. Effect of time on absorbance of Cu(II) - dithiocarbamate complex

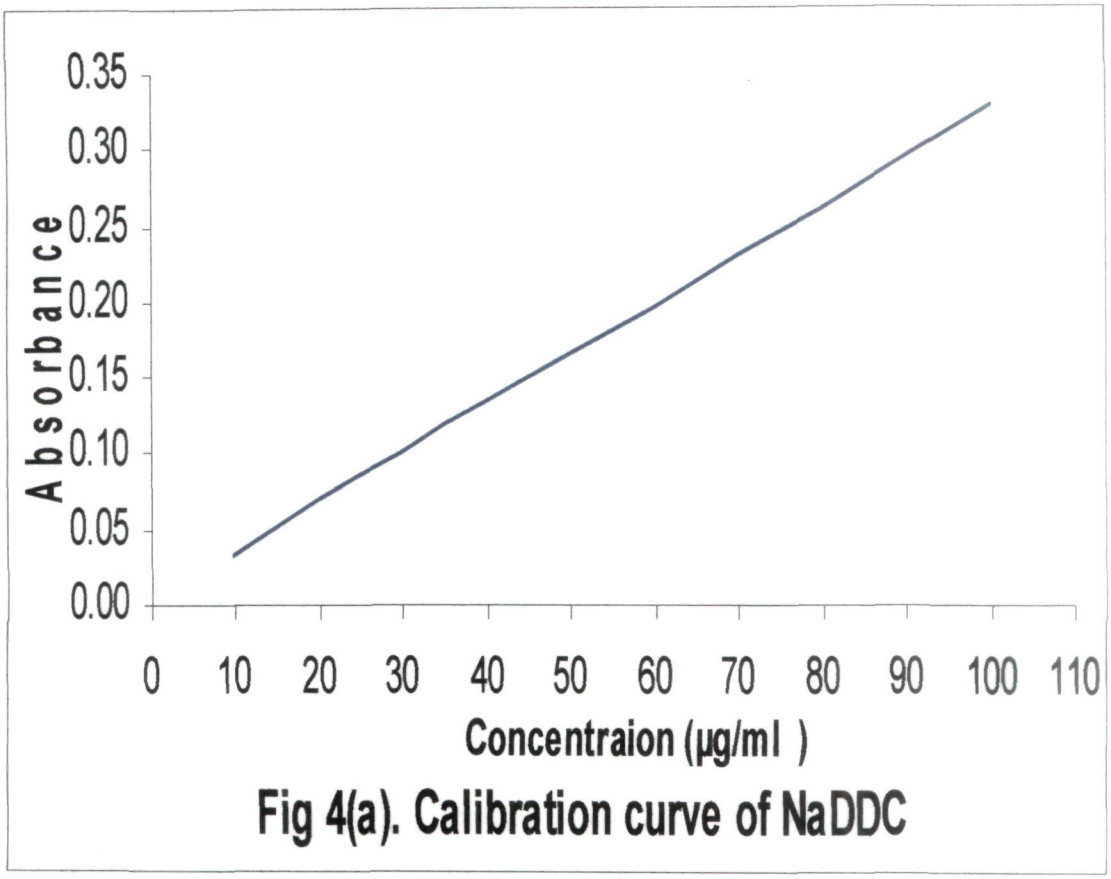

Fig 4(a). Calibration curve of NaDDC

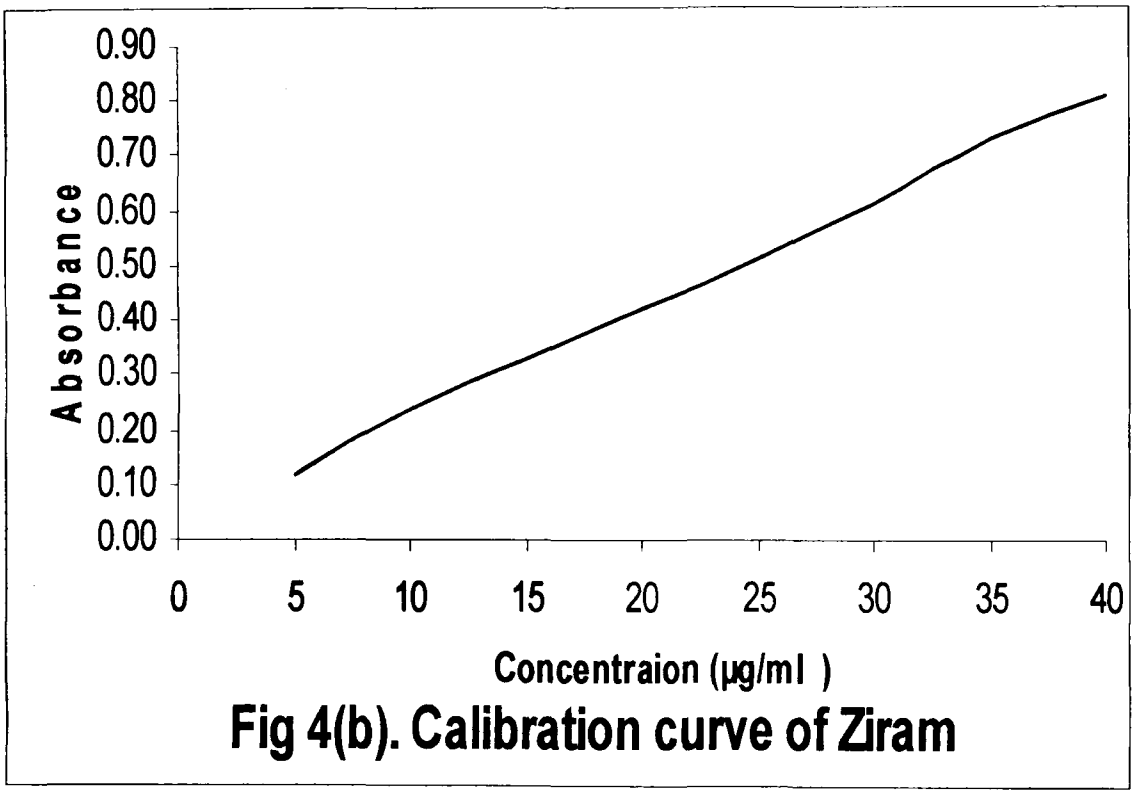

Fig 4(b). Calibration curve of Ziram

TABLE 1: Effect of Foreign Substances

Foreign substance Added		NaDDC		Ziram		% Error	
Name	Amount (µg)	Taken (µg)	Found (µg)	Taken (µg)	Found (µg)	NaDDC	Ziram
Zn^{2+}	500	50	50	10	10.5	0.0	+5.0
Fe^{2+}	500	50	54	10	10	+8.0	0.0
Fe^{3+}	500	50	50	10	10	0.0	0.0
Mn^{2+}	1000	50	50	10	9.5	0.0	-5.0
Ni^{2+}	500	50	50	10	10	0.0	0.0
Pb^{2+}	500	50	54	10	10	+8.0	0.0
Mancozeb	1000	50	47	10	8	-6.0	-20.0
BHC	1000	50	50	10	9.5	0.0	-5.0
Malathion	1000	50	45	10	9.5	-10.0	-5.0

Table 2: Recovery of Ziram from Tap Water

Sample	Fortification Level μgml^{-1}	Amount Recovered μgml^{-1}	Recovery %
Tap Water	5	4.0	80
	10	9.5	95
	12	11.0	92
	14	13.0	93
	16	15.0	93
	18	16.0	89
	20	17.0	85

Table 3: Recovery of Ziram from Grains

Sample	Wheat		pulse		Groundnut	
Forification Level μgml^{-1}	Amount Recovered μgml^{-1}	Recovery %	Amount Recovered μgml^{-1}	Recovery %	Amount Recovered μgml^{-1}	Recovery %
5	5.0	100	4.0	80	2.0	40
10	7.0	70	5.0	50	2.5	25
12	8.0	67	7.0	58	3.0	25
14	8.5	61	8.0	57	3.5	25
16	10.0	63	9.5	60	4.0	25
18	11.5	64	10.5	58	5.0	28
20	15.5	78	13.0	65	6.5	31

Table 4: Determination of Ziram Residues in Formulation

Amount taken μgml^{-1}	Amount found μgml^{-1}	Error %
5	5.0	0.0
10	10.0	0.0
15	13.0	- 13.3
20	19.0	- 5.0
25	22.0	- 12.0
30	28.5	- 5.0
35	34.5	- 1.4
40	39.5	- 1.25

TABLE 5a: Statistical Data for Spectrophotometric Determination of NaDDC

NaDDC (µg)	N	Absorbance at 430nm x±s	C.V	$\bar{D}$	E [(l mol^{-1}) cm^{-1}]
10	5	0.028 ± 0.007	25.0	-0.004	0.05×10^4
20	5	0.050 ± 0.005	8.9	0.000	0.10×10^4
30	5	0.094 ± 0.005	5.3	0.000	0.15×10^4
40	5	0.126 ± 0.005	3.9	0.000	0.22×10^4
50	5	0.144 ± 0.005	3.4	0.000	0.26×10^4
60	5	0.186 ± 0.005	2.7	0.000	0.33×10^4
70	5	0.240 ± 0.00	0.0	0.000	0.41×10^4
80	5	0.258 ± 0.0044	1.7	0.000	0.45×10^4
90	5	0.278 ± 0.0044	1.5	0.000	0.51×10^4
100	5	0.326 ± 0.005	1.5	0.000	0.57×10^4

TABLE 5b: Statistical Data for Spectrophotometric Determination Ziram

Ziram (µg)	N	Absorbance at 430nm X±s	C.V	$\bar{d}$	E [(l mol^{-1}) cm^{-1}]
5	6	0.116 ± 0.0052	4.4	0.66 X 10^{-3}	36.7
10	6	0.235 ± 0.0083	3.5	0.00	73.4
15	6	0.325 ± 0.0055	1.6	0.00	100.9
20	6	0.415 ± 0.0055	1.3	0.00	128.4
25	6	0.513 ± 0.0221	4.3	- 2.3 X 10^{-3}	155.9
30	6	0.608 ± 0.0075	1.2	0.33 X 10^{-3}	186.5
35	6	0.726 ± 0.0081	1.1	0.66 X10^{-3}	223.5
40	6	0.813 ± 0.0245	3.0	20.3 X 10^{-3}	247.7

Table 6: Comparison of Analytical Parameter of the Method under Study with Those of the Reported Method

	Reported method		Cullen[3]	Rao[4]		Rathore[5]	Malik[6]
	Ziram	NaDDC		Ziram	Zineb		
Range ($\mu g\ ml^{-1}$)	5-40	1-10	5-1000	3.04-42.56	2.29-36.64	—	0.63-17.2
λ_{max} (nm)	430	430	430&435	580	580	—	430
Molar Absorptivity ($l\ mol^{-1}cm^{-1}$)	$1.44x10^2$	$0.31x10^4$	—	$7.52x10^4$	$7.52\ x10^4$	—	—
Sandell's Sensitivity ($\mu g\ cm^{-2}$)	0.5	2.0	20 µg of CS_2	0.0040	0.0036	—	—
Standard Deviation	10.83×10^{-3}	4.58×10^{-3}	—	3.5×10^{-3}	8.9×10^{-3}	59.46	—
Coefficient of variance	2.55	5.36	—	1.4	3.7	45.16	—
Average Deviation	2.46	0.0004	—	—	—	—	—
% Error	5.08	7.03	—	—	—	—	—

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